

[00001] BACKGROUND OF THE INVENTION

[00002] This invention relates to insulation for electrical wire or cable.

5 [00003] Wire and cable with dual wall insulation comprising a polyolefin inner layer and polyvinylidene fluoride (PVDF) outer layer have been commercially available for over 30 years. In such insulated products, the adhesion between the polyolefin and PVDF layers is negligible, and as a result the products suffer from the certain disadvantages.

10 [00004] SUMMARY OF THE INVENTION

[00005] It has now been discovered, according to the present invention, that insulation can be provided by a first layer comprising a first polymeric composition which comprises a carbonyl-containing polymer and which is as defined below, and an adjacent second layer
15 comprising a second polymeric composition which comprises a fluoropolymer and which is as defined below, these layers being bonded together by cross-linking. The invention makes it possible to achieve high-performance bonding between such layers while retaining an acceptable balance in the complex relationships of other wire performance requirements.

20 [00006] In a first aspect, this invention provides an insulated electrical wire comprising
1) a metallic conductor, and
2) insulation comprising
(i) a first layer which is composed of a first polymeric composition consisting
of a first polymeric component and optionally a first additive component, the first
25 polymeric component comprising at least 60%, preferably at least 80%, by weight, based on the weight of the first polymeric component of a carbonyl-containing polymer which has a non-aromatic backbone and which may be a homopolymer or copolymer, including terpolymer, the carbonyl-containing polymer comprising repeating units derived from a monomer which (a) can be copolymerized with an
30 olefinic monomer and (b) contains a carboxylic acid ester group, preferably an acrylate or acetate, especially an alkyl acrylate (preferably methyl acrylate, ethyl

acrylate, propyl acrylate or butyl acrylate), the units derived from said monomer constituting at least 5%, preferably at least 9%, more preferably at least 15% , for example 15 to 28%, by weight of the carbonyl-containing polymer and any other repeating units of the carbonyl-containing polymer preferably being derived from an olefinic monomer, preferably ethylene;

(II) a second layer which is in direct contact with the first layer at an interface, and which is composed of a second polymeric composition consisting of a second polymeric component and optionally a second additive component, the second polymeric component comprising at least 50%, particularly at least 90%, for example 100%, by weight based on the weight of the second composition, of polyvinylidene fluoride (PVDF) or a vinylidene chloride (VDF) copolymer consisting essentially of

- (a) repeating units derived from vinylidene chloride, and
- (b) repeating units derived from a partially or fully fluorinated comonomer, preferably hexafluoropropylene (HFP);

the first layer being positioned between the conductor and the second layer.

[00007] In a second aspect, this invention provides an insulated electrical wire comprising

- 1) a metallic conductor, and
- 2) insulation which comprises

(i) a first layer which is composed of a first polymeric composition comprising at least 60%, preferably at least 80%, by weight, based on the weight of the first polymeric composition, of a carbonyl-containing polymer which has a non-aromatic backbone and which may be a homopolymer or copolymer, including terpolymer, the carbonyl-containing polymer comprising repeating units derived from a monomer which (a) can be copolymerized with an olefinic monomer and (b) contains a carboxylic acid ester group, preferably an acrylate or acetate, especially an alkyl acrylate (preferably methyl acrylate, ethyl acrylate, propyl acrylate or butyl acrylate), the units derived from said monomer constituting at least 5%, preferably at least 9%, more preferably at least 15% , for example 15 to 28%, by weight of the carbonyl-containing polymer, and any other

repeating units of the carbonyl-containing polymer preferably being derived from an olefinic monomer, preferably ethylene, and

(ii) a second layer which is in direct contact with the first layer at an interface, and which is composed of a second polymeric composition comprising at least 50%, preferably at least 90%, for example 100%, by weight, based on the weight of the second polymeric composition, of polyvinylidene fluoride (PVDF) or a vinylidene fluoride (VDF) copolymer consisting essentially of

- (a) repeating units derived from vinylidene fluoride, and
- (b) repeating units derived from a partially or fully fluorinated comonomer, preferably hexafluoropropylene (HFP);

the first layer being positioned between the conductor and the second layer.

[00008] Preferably, in each of the first and second aspects of the invention, the layers (i) and (ii), while in contact with each other, have been subjected to conditions which cause cross-linking of polymers at the interface between them, preferably by subjecting the layers to radiation, particularly ionising radiation. The cross-linking is preferably such that at least one of the following conditions is fulfilled

(a) the peel bond strength between the layers, measured by ASTM 81876- 95, is at least 5N, preferably more than 10N,

(b) when a sample of the insulated electrical wire 60 mm long is immersed in a bath of acetone 4.2 mm deep at 23 °C for 1 hour, there is no delamination of the two layers, and

(c) the peel bond strength between the layers after the crosslinking, measured by ASTM B1876-95, is at least 50%, preferably at least 100%, especially at least 500% or 1000%, greater than the peel bond strength between the layers before the crosslinking, measured by ASTM B1876-95.

[00009] A third aspect of the invention provides a method of making an insulated wire or cable, the method comprising the steps of

(A) providing an electrical conductor surrounded by

(i) a first layer which is composed of a first polymeric composition as defined in the first or second aspect of the invention; and

(ii) a second layer which is composed of a second polymeric composition as defined in the first or second aspect of the invention;

5 the first and second layers being in direct contact with each other at an interface, and the first layer being positioned between the conductor and the second layer one; and

(B) exposing the layers while in contact with each other to ionising radiation which causes cross-linking of polymers at the interface.

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[00010] DETAILED DESCRIPTION OF THE INVENTION

[00011] In some embodiments of the invention, the first polymeric component contains, in addition to the carbonyl-containing polymer, polyethylene, preferably high-density polyethylene.

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[00012] Each of the layers (i) and (ii) optionally contains, in addition to the polymeric component of the composition, an additive component to give it required properties.

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[00013] Examples of additives which may be present in the first polymeric composition are cross-linking promoters, antioxidants, pigments, fillers, flame retardants, etc. as known per se. Examples of additives which may be present in the second polymeric composition are cross-linking promoters, pigments, plasticizers, stabilizers, antioxidants and process aids.

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[00014] A convenient method for gauging the bond strength between the layers (i) and (ii), when they have been fabricated onto a wire, is to immerse a sample wire, of total length 60mm, in a bath of acetone (e.g. Fisher Scientific UK, AR certified grade acetone), to a depth of 42 mm. Wires with negligible bonding of the insulation layers experience an extension of the outer layer, along the axis of the wire, that is independent of any extension of the inner layer, and/or wrinkling of the outer layer such that it delaminates from the inner layer in places. When it occurs, the above-mentioned extension of the outer layer typically results in a “tube” extending
30 for 1mm or more beyond the cut end of the inner layer. Wires with significantly bonded

insulation layers experience an extension of both layers without separation, beyond the cut edge of the conductor, along the axis of the wire and/or wrinkling of the two layers together, without delamination. Any such wrinkling of the two layers together can be distinguished from wrinkling only of the outer layer by examining a cross-section of the wrinkles under a microscope.

5 [00015] In the method of the invention, step (A) can make use of any process which causes intimate contact between the layers (i) and (ii). Examples include coating the second polymeric composition onto a pre-formed layer of the first polymeric composition, and dual or multi-walled extrusion to form insulation layers respectively containing one or other of the polymeric compositions. The layers made from the two different compositions can be coextruded, tandem
10 extruded, multipass extruded, or coated by other means. Known wire insulation processes such as tube draw-down extrusion may be used, to form one or more of the layers, but pressure extrusion as known per se is preferred for optimum adhesion of the second and any subsequent insulation layers to be applied to a pre-formed underlying layer. The first layer can optionally be in direct contact with the conductor. The insulation can consist of a first layer as defined and a
15 second layer as defined. The insulation can be, for example, multiple alternating layers of the first and second polymeric composition.

[00016] In step (B) of the method of the invention, the insulation on the wire is exposed to conditions which cause a cross-linking reaction. The cross-linking may involve chemical
20 reagents such as peroxides, but preferably is effected by radiation, especially radiation from a source of ionising radiation capable of causing the formation of free radicals and thus, cross-links, in the polymers, some of which should preferably be formed in the region of the interface between the two compositions. Penetration of the radiation into the insulation at least as far as the interface is therefore desirable, although not necessarily essential if ion or radical mobility, for
25 example, enables molecular reactions to continue at or near the interface after the radiation process. The radiation source could, for example, be a radio-isotope, or an X-ray source, or possibly a non-ionising radical-generating source, for example a UV source, but is preferably an electron beam, more preferably one providing a beam dose greater than 2 Mrads, preferably at least 5 Mrads, more preferably at least 10 Mrads, very preferably at least 15Mrads, into the
30 material.

[00017] It has been found that, when the cross-linking is effected by ionizing radiation, enhancements to the interfacial bond strength may be obtained by including a cross-linking promoter ("pro-rad") in the first and/or second polymeric composition. Known pro-rads may be used, preferably methacrylate/acrylate based pro-rads, e.g. trimethylolpropanetrimethacrylate (TMPTM).

[00018] Experimental results:

[00019] All results quoted in the tables below were obtained by testing pressed plaques of the two materials prepared by the usual polymer handling techniques, well known per se. The plaques were pressed together to bond them face-to-face and the bonded assembly was irradiated as indicated. Plaques were used for these demonstration experiments rather than wires, due to the relative ease of measuring bond strength on plaques. Conditions for these experiments were as follows:

Plaque dimensions: 150mm by 150mm by 0.85mm

Pressing temperature: 200°C

Pressing time: 2 minute preheat, 1 minute at pressure

Pressing pressure: 20-40 Tons over a 300mm by 300mm metal plate

Cooling conditions: 2 minutes between water cooled, 300mm by 300mm, metal plates, at a pressure as above.

[00020] In the Experimental Results shown below, the first composition (comprising the carbonyl-containing polymer) is referred to as the polyolefin-based material and as Material 1, and the second composition is referred to as the PVDF-based material and as Material 2; and the following abbreviations are used (in addition to those already given). EVA is ethylene/vinyl acetate copolymer. VA is vinyl acetate. EEA is ethylene/ethyl acrylate copolymer. EA is ethyl acrylate. EMA is ethylene/methyl acrylate copolymer. MA is methyl acrylate. HDPE is high-density polyethylene. PVDF is polyvinylidene fluoride.

[00021] Example of Effect of Radiation Dose on Bond strength developed between appropriate polyolefin and PVDF-based materials

Material 1	Material 2	Dose(Mrad)	Peel force (N)
EVA copolymer of 25wt% VA content	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	0	0.5
Same as above	Same as above	15	40
EEA copolymer of 15wt% EA content	VDF/HFP copolymer of 10wt% HFP content	0	1
EEA copolymer of 15wt% EA content	VDF/HFP copolymer of 10wt% HFP content	8	24
EEA copolymer of 15wt% EA content	VDF/HFP copolymer of 10wt% HFP content	20	52
Ethylene/acrylic ester/maleic anhydride terpolymer of 19wt% acrylic ester content	VDF/HFP copolymer of 10wt% HFP content	0	<5
Ethylene/acrylic ester/maleic anhydride terpolymer of 19wt% acrylic ester content	VDF/HFP copolymer of 10wt% HFP content	20	21

[00022] Example of Effect of Percentage Comonomer in Ethylene Copolymer Material on bond strength to appropriate PVDF-based material after electron beam crosslinking

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Material 1	Material 2	Dose(Mrad)	Peel (N)
EMA copolymer with 9wt% MA content	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	20	4
EMA copolymer with 28wt% MA content	Same as above	20	45

[00023] Example of Effect of percentage Copolymer in a polyolefin polymer blend on bond strength with appropriate PVDF-based material after electron beam crosslinking

Material 1	Material 2	Dose(Mrad)	Peel force (N)
100% HDPE	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	20	0
20% HDPE + 80% EEA copolymer of 15wt% EA content	Same as above	20	70

[00024] Example of Effect of PVDF-based material type on bond strength with appropriate polyolefin based material after electron beam crosslinking

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Material 1	Material 2	Dose(Mrad)	Peel (N)
EVA copolymer with 25wt% VA content	PVDF homopolymer	15	4
As above	VDF/HFP copolymer of 10wt% HFP content	15	17.5

[00025] Example of Effect of the addition of Pro-rad in Olefinic Material on bond strength with appropriate PVDF-based material after electron beam crosslinking

Material 1	Material 2	Dose(Mrad)	Peel (N)
20% HDPE + 80% EEA copolymer of 15wt% EA content	VDF/HFP copolymer of 10wt% HFP content +7.5wt% additives	20	70
19% HDPE + 77%EEA copolymer of 15wt% EA content + 4% TMPTM pro-rad	Same as above	20	>130

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[00026] Examples of Wire Construction

[00027] An electrical wire in which the insulation consists of two polymeric layers bonded together according to the present invention was made as follows:

5 [00028] The inner layer of insulation (i.e. nearer to the wire conductor) was a polyolefin-based material, consisting predominantly of (a) an EEA copolymer containing 15wt% EA and (b) HDPE in a weight ratio of approximately 8:2 copolymer:HDPE, with usual other additives present in smaller proportions including crosslinking promoters, stabilisers, antioxidants, pigments and process aids at a total level of 24wt%. This layer was pressure extruded onto the
10 metallic conductor.

[00029] The outer layer of insulation consisted predominantly of a PVDF/HFP copolymer containing 10wt% HFP, which in this example contains a crosslinking promoter, and other known additives such as pigments, plasticisers, stabilisers, antioxidants and process aids in usual
15 proportions totalling 7.5wt%. This outer layer was pressure extruded in a separate operation onto the pre-formed inner layer. This coated wire product was then passed through an electron beam, and received a radiation dose of 20Mrads.

[00030] In a second example a wire was made as above, in which the crosslinking
20 promoter in the inner layer was 4% TMPTM, and the outer layer of insulation was comprised solely of the PVDF/HFP copolymer containing 10wt% HFP. This coated wire product was then passed through an electron beam, and received a radiation dose of 20 Mrads. This wire was subjected to the acetone immersion test, confirming that the insulation layers were significantly bonded together.

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[00031] In a third example, a wire of the same construction as the second example was made by tandem pressure extrusion of the inner and outer insulation layers. This coated wire product was then passed through an electron beam, and received a radiation dose of 20 Mrads. This wire was subjected to the acetone immersion test, confirming that the insulation layers were
30 significantly bonded together.

[00032] Demonstration of Improved performance of wires constructed as in the second example above, relative to current commercially available wire.

[00033] A wire of the above construction and manufacturing process (designated wire A) was compared with a market leading commercially available polyolefin/PVDF dual-walled wire (designated wire B) of the same dimensions, over a range of tests for wire robustness relevant to harsh handling and end-use environments. The following results were obtained.

10 [00034] Example of scrape abrasion resistance improvement.

[00035] Method: Equipment=conventional type wire scrape abrader, wire size 0.75mm²(conductor cross sectional area), blade type flat, width 3.5mm held perpendicular to wire, with 0.05mm radius edges each side, applied load 1.8kg, stroke length 10cm, at 55 cycles/minute

Wire Type	No. of scrape cycles to abrade through PJ at 40°C
A	>800
B	272

Wire Type	No. of scrape cycles to abrade through PJ at 5°C
A	>1350
B	212

[00036] Example of cold impact resistance improvement.

20 [00037] Method: wire size 6mm²(conductor cross sectional area), impact weight 800g, drop height 275mm onto anvil, anvil area impacting on wire of dimensions 7mm x 2mm widening to 3.4mm via 45° taper each side, ambient temperature 5°C. Visual detection of insulation crack propagation.

Wire Type	Result of cold impact test
A	No cracks in PJ propagate away from site of anvil impact
B	Severe cracks in PJ, >5 mm in length, propagate away from site of anvil impact. PJ starts to peel off core

[00038] Example of solvent resistance improvement.

[00039] Method: wire size 0.75mm^2 , length of wire 60mm, acetone immersion length 75%
 5 of wire length, immersion time 1 hour, temperature 23°C

Wire Type	Result of acetone immersion test
A	No separation/delamination of core and PJ, no cracking of either insulation layer observed
B	PJ wrinkled very severely along immersed length, cracking spontaneously in two places, and exposing 2-3mm of core